

# A Study of Silicon Nanoparticles with Applications to Medical Resonance Imaging

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## Introduction:

Nuclear magnetic resonance imaging (MRI) is a non-invasive medical imaging technique that uses a magnetic field to align protons in the body. By combining field gradients and radiofrequency excitation, three-dimensional images of proton density and nuclear spin lattice relaxation times (T1s) can be created [1]. The use of silicon (Si) nanoparticles as an imaging agent provides an alternative to conventional proton imaging that allows sensitive targeted imaging. They are hyperpolarizable [2], non-toxic and using silicon minimizes background noise problems because it is found in insignificant amounts in the body. T1 determines the time it takes for the nuclear polarization to return to its original orientation aligned with the field, and so determines the length of time that pre-hyperpolarized particles will be able to be imaged once injected into the body.

Various-sized crystalline nanoparticles were fabricated by ball-milling high resistivity ( $> 30 \text{ k}\Omega\text{cm}$ ) Si wafers. These particles were separated by centrifugation into different size distributions—confirmed by scanning electron microscopy (SEM). Hydrogen has been shown to passivate surface states at the Si/SiO<sub>2</sub> interface in nanocrystals [3]. We saw hydrogen passivation as a possible method to reduce imperfections and consequently increase T1. The nanoparticles were annealed (Jiplec Rapid Thermal Processor) under a forming gas mixture of 3% hydrogen and 97% nitrogen for 1 and 10 minutes at 350°C. Commercially available crystalline and amorphous nanoparticles were studied in the same manner for comparison.

## Experiment:

Silicon Quest boron-doped wafers were ground using mortar and pestle. The shards were massed to 9.6 grams using a digital balance and spun in a Retsch ball mill with ten, 1 cm diameter zirconium oxide balls for 10 minutes dry and then together with 20 mL of anhydrous ethanol for 4 more hours. The 1 cm balls were replaced with 40 grams of 2 mm diameter zirconium oxide balls and milled again for between 8 and 26 hours depending on the desired final nanoparticle size. The solution was sonified at 25% for 10 minutes in a Bronson Digital Sonifier and aliquotted into four 50 mL test tubes.

$$V_s = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2$$

Equation 1: Stoke's Law.

The behavior of small spherical objects in solution can be described using Stoke's Law (Equation 1). Using this, we created a model to predict the expected size of particles remaining in solution after being spun in the centrifuge [4]. Stoke's Law has:  $V_s$  = the particles' settling velocity (m/s),  $g$  = the acceleration ( $\text{m/s}^2$ ),  $\rho_p$  and  $\rho_f$  = the mass densities of the particles and the fluid ( $\text{kg/m}^3$ ),  $\mu$  = the fluid's dynamic viscosity (in Pa s) and  $R$  = the particle diameter. The input parameters for our algorithm include the height of solution in tube compared to the radius of the centrifuge, revolutions per minute in the centrifuge, and time in seconds.

Centrifuge tubes were filled to 37.5 mL and spun for a time and speed determined by our model. Particles sized greater than our desired upper cutoff would be spun to the bottom of the tube (the pellet). The remaining liquid (supernatant) was poured out into a round bottom flask. The tube with pellet was filled with ethanol, sonified at 25% for 3 minutes and

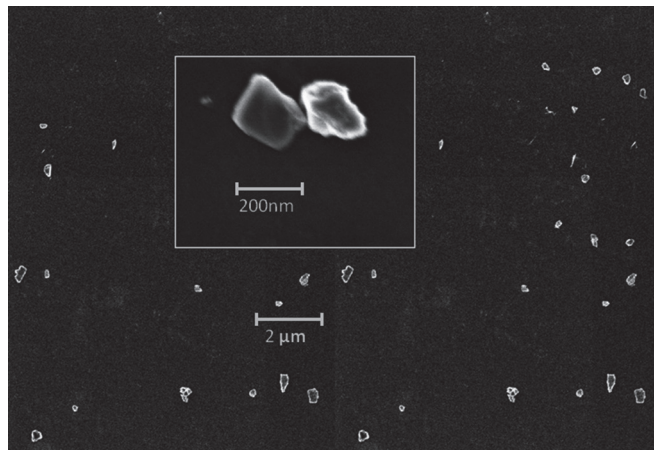


Figure 1: Sample SEM image of silicon nanoparticles average size 150 nm.

spun at the same parameters before pouring the supernatant out into the same flask. This whole procedure was repeated a third time. Then the supernatant was condensed using a rotary evaporator (Buchi) and divided into two test tubes, again at 37.5 mL. These tubes were spun such that sizes less than our lower cutoff would remain in the supernatant. This left a pellet of particles with sizes within the two estimated cutoffs. The supernatant was removed and replaced with ethanol. The tubes were spun for the lower limit six more times. The nanoparticle distributions were verified by scanning electron microscopy (see Figure 1). These procedures were also successfully applied to commercial nanoparticles.

We then annealed dried nanoparticles and characterized them using NMR spectroscopy. Approximately 0.5 g of dried particles were placed on a silicon wafer and tests were done in forming gas (3% hydrogen, 97% nitrogen) and also in pure nitrogen as a control. Time was varied from 1 to 10 minutes for heat (350°C) and gas exposure.

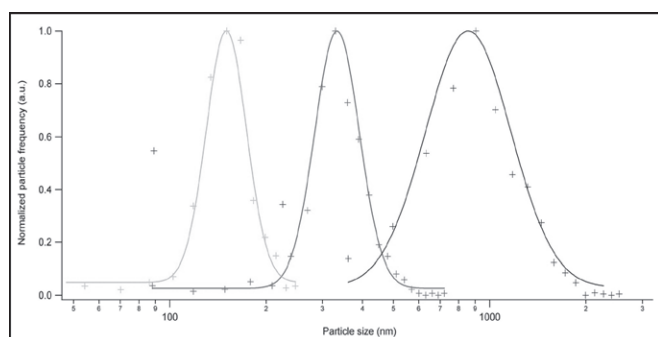


Figure 2: Normalized distributions of particles with average sizes of 150 nm, 350 nm, and 1000 nm.

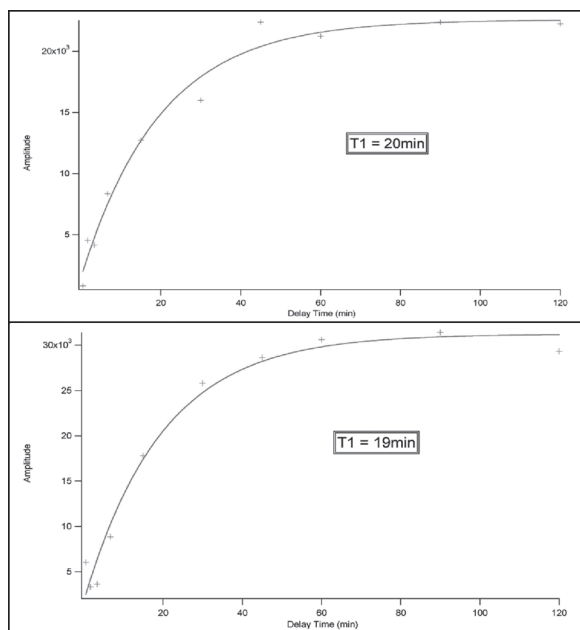


Figure 3: T1 measurements of forming gas annealed (a) and control (b) nanoparticles sourced commercially (American Elements).

## Results/Discussion:

Using the model we developed, we were able to obtain non-overlapping size distributions of particles using centrifugal separation, as shown in Figure 2. T1 measurements by NMR showed no increase after any of the tested annealing procedures, for either controlled-size or commercially available products (see Figure 3).

## Conclusions:

We have developed a repeatable procedure for centrifugal size separation that works on both on commercially synthesized and top-down fabricated silicon nanoparticles. Although some errors may have resulted from the use of two different NMR magnets and exposure to air, we believe that these factors would not have overshadowed any real improvement in T1 by annealing in forming gas. The ability to control size distributions of silicon nanoparticles is an important step in understanding the NMR properties of these particles, and also their impact on biological systems.

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